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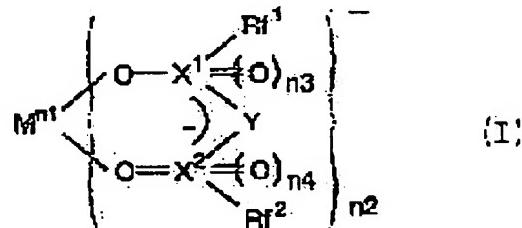
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(54) PHOTO-FUNCTIONAL MATERIAL MADE BY USING RARE EARTH ELEMENT COMPLEX, AND LIGHT EMITTING DEVICE

(57)Abstract:

PROBLEM TO BE SOLVED: To prepare a highly color rendering white light emitting device by combining a semiconductor light emitting device with a transparent wavelength conversion medium covering it, and a device for emitting light of an arbitrary color.

SOLUTION: For example, a first complex having a constitution of formula (I) (wherein n1 is 2 or 3; n2 is 2, 3 or 4; Rf1 and Rf2 are each a hydrogen-free 1-22C aliphatic group or the like; X1 and X2 are each a group VIA element except for O, or the like; n3 and n4 are each 0 or 1; and Y is N or the like), with the central ion M comprising Eu, and a second complex having the same constitutional formula, with the central ion comprising Tb are incorporated into a solid carrier comprising e.g. a transparent film, which is combined with a semiconductor light emitting device capable of emitting a blue light in the region of light emitted by the excited Eu and Tb.



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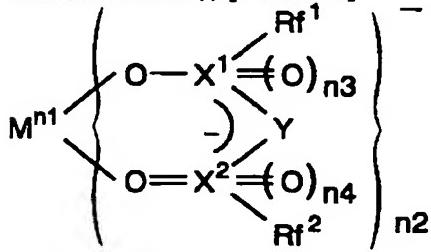
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CLAIMS

[Claim(s)]

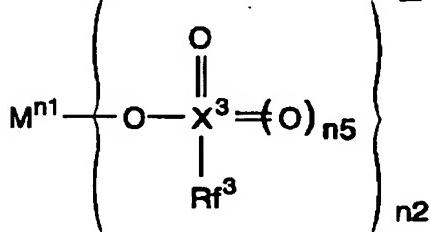
[Claim 1] The optical functional material which has the structure expression of either a general formula (I) – (VII), and consists of the transparency solid support which contains the 1st complex whose central ion M is Eu, and the 2nd complex whose central ion M it has the structure expression of either a general formula (I) – (VII) similarly, and is Tb together.

General formula (I) [Formula 1]



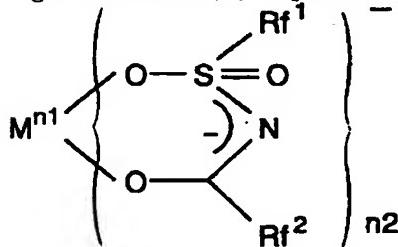
(In this formula, n1 shows 2 or 3.) n2 shows 2, 3, or 4. Rf1 and Rf2 show the same or the heterocycle radical which does not contain the different aromatic series radical or different hydrogen atom which does not contain the aliphatic series radical of C1-C22 which do not contain a hydrogen atom, and a hydrogen atom. X1 and X2 show either the same, or a different IVA group atom, VA group atom except nitrogen and the VIA group atom except oxygen. n3 and n4 show 0 or 1. Y shows C-Z' (Z' shows the aliphatic series radical of C1-C22 which do not contain heavy hydrogen, a halogen atom, or a hydrogen atom). N, P, As and Sb, or Bi. However, when X1 is a carbon atom, n3 is 0, when X2 is a carbon atom, n4 is 0 and, in the case of a carbon atom, X1 and X2 are the aromatic series radicals in which at least one side of Rf1 and Rf2 does not contain a hydrogen atom simultaneously.

General formula (II) [Formula 2]



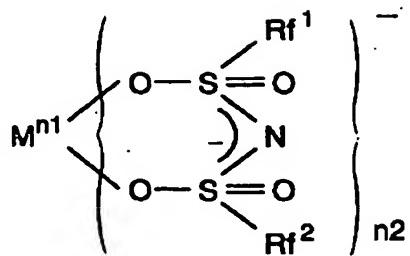
(In this formula, n1 and n2 are as aforementioned.) Rf3 shows the heterocycle radical which does not contain the aromatic series radical or hydrogen atom which does not contain the aliphatic series radical of C1-C22 which do not contain a hydrogen atom, and a hydrogen atom. X3 shows the IVA group atom except carbon, VA group atom except nitrogen, or the VIA group atom except oxygen. n5 shows 0 or 1.

a general formula (III) — [Formula 3]



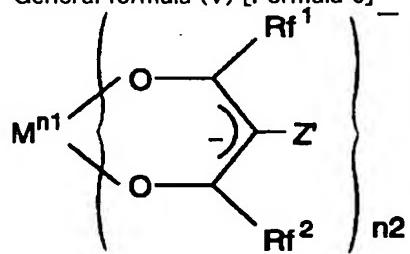
(In this formula, Rf1, Rf2, n1, and n2 are as aforementioned.)

General formula (IV) [Formula 4]



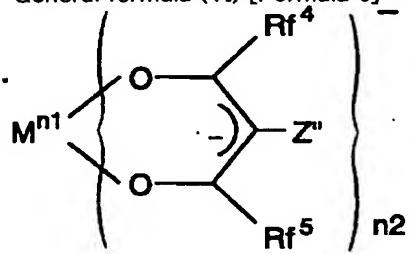
(In this formula, Rf^1 , Rf^2 , $n1$, and $n2$ are as aforementioned.)

General formula (VI) [Formula 6]



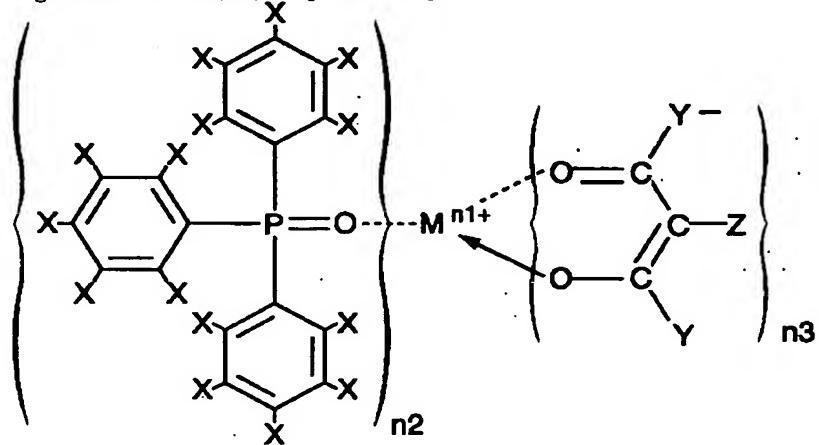
(In this formula, Rf^1 , Rf^2 , $n1$, $n2$, and Z' are as aforementioned.)

General formula (VII) — [Formula 7]



(In this formula, $n1$ and $n2$ are as aforementioned.) Z'' shows a hydrogen atom or Z' (Z' the aforementioned passage). Rf^4 and Rf^5 show the same or the heterocycle radical which does not contain the different aromatic series radical or different hydrogen atom which does not contain the aliphatic series radical of C1-C22 which do not contain a hydrogen atom, and a hydrogen atom.

a general formula (VII) — [Formula 7]



(In this formula, $n1$ shows 2 or 3.) $n2$ shows 1 or 2. $n3$ shows 1, 2, 3, or 4. X shows the same or a different hydrogen atom, a heavy hydrogen atom, a halogen atom, the radical of C1-C20, a hydroxyl group, a nitro group, the amino group, a sulfonyl group, a cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulfhydryl group. Y shows the same or a different radical of C1-C20, a hydroxyl group, a nitro group, the amino group, a sulfonyl group, cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulfhydryl group. Z shows a hydrogen atom or a heavy hydrogen atom.

[Claim 2] The optical functional material which carried out the laminating of the transparency fixed support which has the structure expression of either a general formula (I) according to claim 1 — (VII), and contains the 1st complex whose central ion M is Eu, and the transparency solid support which similarly has the structure expression of either a general formula (I) according to claim 1 — (VII), and contains the 2nd complex whose central ion M is Tb.

[Claim 3] Furthermore, the optical functional material according to claim 1 with which the above-mentioned transparency fixed support has the structure expression of either a general formula (I) — (VII), and also contains the 3rd complex whose central ion M is Tm.

[Claim 4] The transparency fixed support which has the structure expression of either a general formula (I) according

to claim 1 – (VII), and contains the 1st complex whose central ion M is Eu, The transparency solid support which similarly has the structure expression of either a general formula (I) according to claim 1 – (VII), and contains the 2nd complex whose central ion M is Tb, The optical functional material which carried out the laminating of the transparency solid support which similarly has the structure expression of either a general formula (I) according to claim 1 – (VII), and contains the 3rd complex whose central ion M is Tm.

[Claim 5] Luminescence equipment characterized by combining an optical functional material according to claim 1 to 4, and the light emitting diode or the semiconductor laser which emits the excitation light corresponding to the excitation wavelength range of each above-mentioned central ion.

[Claim 6] Luminescence equipment according to claim 5 characterized by the above-mentioned excitation light having the wavelength corresponding to f-f transition of each above-mentioned central ion.

[Claim 7] So that the light which doubled luminescence of the 1st complex, luminescence of the 2nd complex, and luminescence of the above-mentioned excitation light source may become white So that the light which doubled luminescence of the 1st complex, luminescence of the 2nd complex, and luminescence of the 3rd complex may become white Or concentration of the 1st complex in a transparency solid support and concentration of the 2nd complex, Or luminescence equipment according to claim 5 or 6 characterized by adjusting the concentration of the 1st complex, the concentration of the 2nd complex, the concentration of the 3rd complex, or the thickness of each transparency fixed support layer.

[Claim 8] Luminescence equipment according to claim 5 to 7 characterized by the above-mentioned light emitting diode or semiconductor laser having the luminous layer expressed with general formula $In_xGa_{1-x}N$ ($0 < x < 1$).

[Claim 9] Luminescence equipment according to claim 1 to 8 characterized by the above-mentioned transparency solid support being transparency resin.

[Claim 10] Luminescence equipment according to claim 1 to 9 characterized by the mean particle diameter with which the above-mentioned transparency solid support supported the above-mentioned complex containing the complex (host-guest) of nano size.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the luminescence equipment which combined the optical functional material which consists of the wavelength conversion matter containing the organic fluorescent substance which consists of a rare earth complex, and the light emitting diode or the semiconductor laser which excites this organic fluorescent substance. The luminescence equipment concerning this invention can use the high source of the white light or arbitration color of color rendering properties as luminescence equipment which can emit light.

[0002]

[Description of the Prior Art] One of the descriptions of light emitting diode (LED) is a thing with high (that is, the spectrum full width at half maximum is narrow) monochromaticity. The full color display which carried out array mounting of the LED emitter which consists of a (Red R) green (G) blue (B) color in all directions on the flat surface is already widely used using this description. In this case, the foreground color is controlled by the intensity ratio of RGB each color to arbitration.

[0003] However, when it sees not as a display but as a lighting system, many problems are still left behind to LED. As mentioned above, although the white light can also be acquired by using the equipment which arranged the LED emitter of RGB and setting up the intensity ratio of RGB each color suitably When it sees as a lighting system, as compared with the incandescent lamp and fluorescent lamp which are the conventional lighting system, there are problems, like that (1) (3) which must control independently (2) RGB each color by which mixture in three primary colors will be checked by looking if it sees finely equipment becomes large-scale, and (4 "color rendering properties") is bad.

[0004] "Color rendering properties" means the property of the light source whether a body is visible to what kind of color here, when a body is illuminated by the light source. In view of the importance of the color rendering properties in a lighting system, CIE (Commission Internationale de l'Eclairage, Commission Internationale de l'Eclairage) defined the color-rendering-properties assessment approach in 1964. According to this, the series of the criteria light source which can be chosen with the color temperature of the light source for assessment is defined, and a color rendering index Ra is defined from the color gap when illuminating a regular trial color by the criteria light source and the light source for assessment. A color rendering index Ra takes the value of 0-100, and the light source's for assessment corresponds with the criteria light source in how whose color is visible at the time of 100. As the criteria light source, color temperature 5000K or less, when exceeding 5000K for a full radiator, the calculated value (it is called the synthetic daylight) of the spectral distribution of the daylight is used. Eight colors which have a predetermined spectral reflectance as an object for general as a trial color are chosen, and the color rendering index calculated by this is called a general color rendering index. In addition, seven colors are chosen as an object for the special objects, and Japanese flesh color is contained in it. The color rendering index calculated by this is called a special color rendering index. Furthermore, please refer to "illuminating engineering" for details (from the edited by Institute of Electrical Engineers of Japan, the Ohm-Sha **, and p.36).

[0005] It is based on the light of a full radiator in the case of color-rendering-properties assessment because the natural light (sunlight) is close to the light of a full radiator. The light of each wavelength is continuously contained in the light which a full radiator emits. Since the hue of an object is determined by the rate of a light reflex for every wavelength of an object (spectral reflectance), if the intensity distribution are [that the light of each wavelength is contained continuously] close to it of a full radiator in the spectral distribution of the illumination light (emitter), how whose color of an object is visible will become a thing near it under the natural light. However, even if the LED white emitter constituted from RGB makes the white light emit light as the whole by adjusting the intensity ratio of each color even if, the spectral distribution are discontinuous things which have the peak of narrow width of face only in three waves of parts, R (red), G (green), and B (blue), rather than are continuous. Because of this discontinuity, a RGB-LED emitter cannot have color rendering properties sufficient as a lighting system.

[0006] As the light source for white lighting using single LED, what (or it applied) covered current and gallium nitride system blue LED with the YAG fluorescent substance is devised (refer to JP,5-152609,A official report). This carries out optical pumping of the YAG fluorescent substance using the blue glow (wavelength of 460nm) from the InGaN barrier layer of gallium nitride system blue LED, and acquires the white light with the color mixture of the yellow luminescence and the blue from LED which are the fluorescence from the fluorescent substance.

[0007] The spectrum of white LED (correlated color temperature: 6500K) which consists of gallium nitride system blue LED which applied the YAG fluorescent substance to drawing_1 , and the spectrum of the standard light D65 (correlated color temperature: 6504K) are shown. The standard light D65 is the standard light for color rendering assessment representing the daylight of color temperature 6504K here, and it is set by CIE by statistics processing of the actual measurement of natural daylight spectral distribution. As compared with the standard light D65 for color rendering assessment, as for the spectrum distribution of white LED, the spectrum distribution of a purple - purple-blue field, a bluish green - green field, and a red field is low. Although the color rendering index of white LED is shown in drawing_2 , corresponding to spectrum distribution, it turns out are purple-blue and that the special color rendering index of green and red is inferior. therefore, the field to apply -- it is necessary to reinforce the spectrum component needed with a certain form, and to raise the color rendering properties of an object

[0008] On the other hand, also in the white LED technique by the blue and the YAG fluorescent substance of the conventional technique, a color temperature is controllable by the increase of coverage, or carrying out and changing of a YAG fluorescent substance] the luminescence component (the amount of illuminants) from a fluorescent

substance (refer to drawing 5). However, when the color temperature used with the sufficient actual condition makes the luminescence component from [from the 6500K neighborhood] a fluorescent substance increase and makes a color temperature low, the following two troubles exist.

(1) Since the fluorescence effectiveness of a YAG fluorescent substance is about 20%, the more it strengthens the luminescence component from a YAG fluorescent substance, the more the luminous efficiency as white LED will fall. (2) since a YAG fluorescent substance has the weak color component with it, yellowness is strong and its red color rendering properties are bad — unnatural — it will be white. [a strong yellow component and] [red]

[0009] A medical applicable field is described as an example. In the sea hospital in September 11, 2000 and Kyoto prefectural Yosa, the first surgical operation (internal shunt construction way to a chronic-renal-failure patient) was performed, and it succeeded in the world using a white LED lighting system. This lighting system arranges in the shape of an array the white LED chip which consists of gallium nitride system blue LED which applied the YAG fluorescent substance, uses it as an illuminant panel, and this is mounted in plastics goggles and it produces it. This operation was conducted by obtaining sufficient illuminance under dc-battery actuation, and the usefulness of white LED is proved [operation] as a handy lighting device which a surgeon can carry.

[0010]

[Problem(s) to be Solved by the Invention] However, it was pointed out about the color rendering properties of white LED at the time of the above-mentioned operation that it is hard to recognize the blood vessel (blackish red) of an artery (clear red) and a vein. This is because a problem is in the color rendering properties in the red field of used white LED, and is considered that the reddish spectrum of orange or a 640-780nm red field which is 597-640nm is solvable by strengthening.

[0011] As a means which strengthens the spectrum of a red field, distributing the AlGaInP system LED or the AlGaAs system LED in all directions on a flat surface in a white LED chip is considered first. However, in order to mix an emission spectrum uniformly within a radial plane, it will be necessary to distribute mounting of a chip uniformly as densely as possible, or to mount a diffusion plate in an LED emitter panel front face. And the reinforcement of white LED (YAG fluorescent substance spreading-gallium nitride system blue LED) and red LED (the AlGaInP system LED or the AlGaAs system LED) must be controlled independently.

[0012] The easiest approach of strengthening the spectrum of a red field, without producing the above-mentioned problem is applying to the present white LED the fluorescent substance which emits light in a red field. However, when aimed at the lighting system generally used widely, moreover as the red fluorescent substance, it becomes indispensable requirements with a well head that it is extremely stable. And the point that workability is high, and the points which do not contain matter which pollutes earth environment even if abandoned excluding a poisonous component to the body are also important requirements.

[0013] As a fluorescent substance of a red field, if organic molecule ingredients, such as a rhodamine, are used, high luminous efficiency will be acquired, but since decomposition and **** arise easily by optical exposure, it is not suitable for practical use. The ZnCdS:Ag system and the Y2O2 S:Eu3+ system fluorescent substance are used as a Braun-tube red fluorescent substance (electron beam pumping) of television, and comparatively high red conversion is obtained by the LED light source (360-380nm) of an ultraviolet area. However, since conversion efficiency sufficient in blue excitation is not acquired, it is uncombinable with white LED (YAG fluorescent substance spreading-gallium nitride system blue LED) used now. if the present luminous efficiency ultraviolet [LED] is markedly alike as compared with blue LED and considers a low point, the combination with this practical will not become. And long term stability is obtained only within the Braun tube stopped by the vacuum, in the environment in atmospheric air, moisture absorption arises, photochemical reaction is accelerated and the problem that degradation of a fluorescent substance occurs produces these fluorescent substances. The closure technique for solving this is not yet developed. Furthermore, the ZnCdS:Ag system contains Cd and it is apprehensive about the effect on an environment.

[0014] Considering such a thing, about the red fluorescent substance in which the present white LED and combination are possible, the fluorescent substance developed so far has various problems.

[0015] Fluorescence ingredients various by adding rare earth metals, such as Eu (europium), Tb (terbium), and Tm (thulium), in matter, such as an inorganic oxide and inorganic sulfide, conventionally have been developed. However, conventionally, "A rare earth metal could not emit light easily in an organic medium" was presupposed, and the luminous efficiency of the rare earth metal in the inside of organic media, such as a plastics system, was actually dramatically lower than the energy gap theory of quantum physics till recent years.

[0016] on the other hand, the thing for which some these artificers are begun from re-evaluation of the energy gap theory — a group of rare earth metals, such as neodymium which can emit light in an organic medium for the first time in the world in 1995, — it succeeded in the design of a complex (the Hasegawa ****, "how the neodium which does not shine in an organic medium to be shone", chemistry, industry, volume [53rd] (2000) No. 2, and pp.126-130). Patent application was also performed about these parts (PCT/JP98/00970=WO98/40388 official report, a Japanese-Patent-Application-No. 10-238973=JP,2000-63682,A official report, Japanese-Patent-Application-No. 11-62298= JP,2000-256251,A official report).

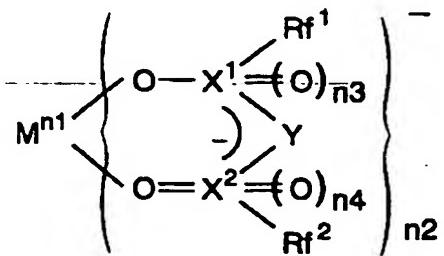
[0017] These complexes are stable also in the elevated temperature of 350 degrees C, it is hard to produce photodegradation, and an organic compound reverses the conventional common sense of being easy to produce degradation by heat or optical exposure. Moreover, compatibility with the host ingredient of a resin system called plastics and a polymer is also high, and becoming easy workability with a next-generation light corpuscle child conjointly is expected.

[0018] First of all, this invention realizes the high white luminescence equipment of color rendering properties by choosing and using the matter suitable for especially the object in these complexes. Moreover, it is also possible for this invention not to stop at mere white luminescence equipment, but to use light of an arbitration color as the equipment which emits light.

[0019]

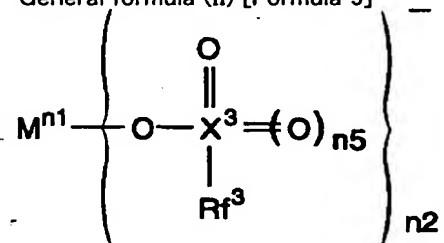
[Means for Solving the Problem] The optical high-performance material concerning this invention accomplished in order to solve the above-mentioned technical problem has the structure expression of either the following general formula (I) - (VII), and is characterized by consisting of the transparency solid support containing the 1st complex whose central ion M is Eu (europium), and the 2nd complex whose central ion M it has the structure expression of either a general formula (I) - (VII) similarly, and is Tb (terbium).

General formula (I) [Formula 8]



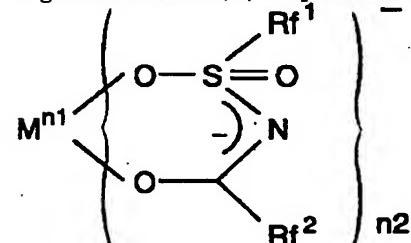
(In this formula, n1 shows 2 or 3.) n2 shows 2, 3, or 4. Rf1 and Rf2 show the same or the heterocycle radical which does not contain the different aromatic series radical or different hydrogen atom which does not contain the aliphatic series radical of C1-C22 which do not contain a hydrogen atom, and a hydrogen atom. X1 and X2 show either the same, or a different IVA group atom, VA group atom except nitrogen and the VIA group atom except oxygen. n3 and n4 show 0 or 1. Y shows C-Z' (Z' shows the aliphatic series radical of C1-C22 which do not contain heavy hydrogen, a halogen atom, or a hydrogen atom), N, P, As and Sb, or Bi. However, when X1 is a carbon atom, n3 is 0, when X2 is a carbon atom, n4 is 0 and, in the case of a carbon atom, X1 and X2 are the aromatic series radicals in which at least one side of Rf1 and Rf2 does not contain a hydrogen atom simultaneously.

General formula (II) [Formula 9]



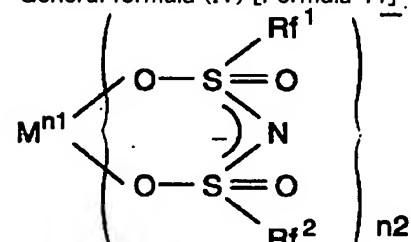
(In this formula, n1 and n2 are as aforementioned.) Rf3 shows the heterocycle radical which does not contain the aromatic series radical or hydrogen atom which does not contain the aliphatic series radical of C1-C22 which do not contain a hydrogen atom, and a hydrogen atom. X3 shows the IVA group atom except carbon, VA group atom except nitrogen, or the VIA group atom except oxygen. n5 shows 0 or 1.

a general formula (III) — [Formula 10]



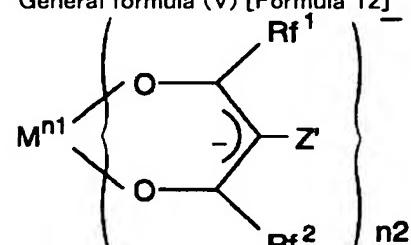
(In this formula, Rf1, Rf2, n1, and n2 are as aforementioned.)

General formula (IV) [Formula 11]



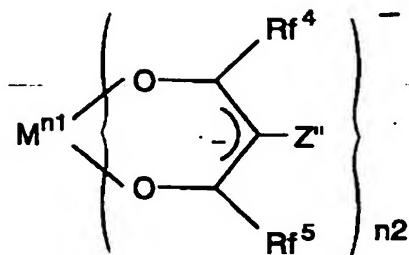
(In this formula, Rf1, Rf2, n1, and n2 are as aforementioned.)

General formula (V) [Formula 12]



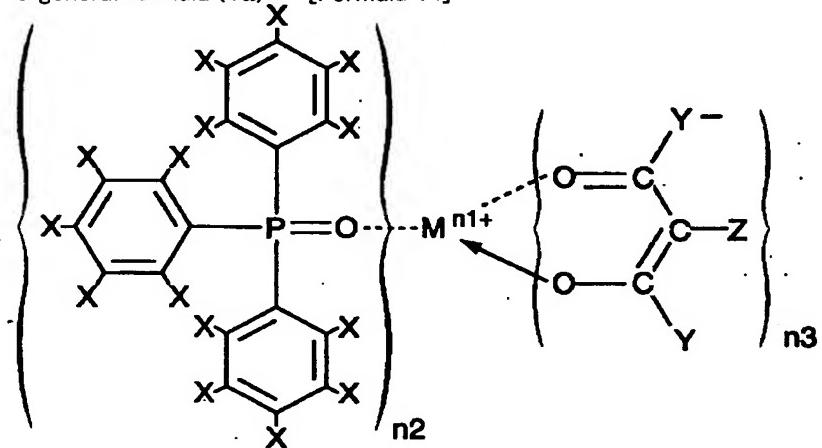
(In this formula, Rf1, Rf2, n1, n2, and Z' are as aforementioned.)

General formula (VI) [Formula 13]



(In this formula, n1 and n2 are as aforementioned.) Z'' shows a hydrogen atom or Z' (Z' is the same as the above). Rf⁴ and Rf⁵ show the same or the heterocycle radical which does not contain the different aromatic series radical or different hydrogen atom which does not contain the aliphatic series radical of C1-C22 which do not contain a hydrogen atom, and a hydrogen atom.

a general formula (VII) — [Formula 14]



(In this formula, n1 shows 2 or 3.) n2 shows 1 or 2. n3 shows 1, 2, 3, or 4. X shows the same or a different hydrogen atom, a heavy hydrogen atom, a halogen atom, the radical of C1-C20, a hydroxyl group, a nitro group, the amino group, a sulfonyl group, a cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulfhydryl group. Y shows the same or a different radical of C1-C20, a hydroxyl group, a nitro group, the amino group, a sulfonyl group, cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulfhydryl group. Z shows a hydrogen atom or a heavy hydrogen atom.

[0020] In addition, in addition to these 1st complexes and the 2nd complex, it has the structure expression of either the same general formula (I) – (VII), and the 3rd complex whose central ion M is Tm (thulium) may be added. When this 3rd complex is added, the light source of a near-ultraviolet region is used as the excitation light source, and the 1st – the 3rd complex are made to emit light simultaneously.

[0021] General formula (I) Since the aliphatic series radical of C1-C22 which do not contain the hydrogen atom of – (VI), the aromatic series radical which does not contain a hydrogen atom, the heterocycle radical which does not contain a hydrogen atom, and the example of X1, X2, and X3 are indicated by [0031] – [0037] of a JP,2000-63682,A official report, refer for them there to. Moreover, the synthesis method of the above-mentioned complex is also indicated by [0047] – [0067] of this official report.

[0022] In addition, in these rare earth complexes, Rf¹ and Rf² are good in respect of compatibility with plastics and the polymer whose thing to C1 or about two C is the below-mentioned transparency solid support, and they generate a polymer with stable CF₃ or CF₂CF₃ especially also in it.

[0023] Also about the complex expressed with a general formula (VII), the detail is indicated by [0012] – [0021] of an application for patent 2001-272547, and the synthesis method is indicated by [0024] – [0027].

[0024]

[Embodiment of the Invention] Eu is the element of the atomic number 63 belonging to a lanthanoids, by designing a ligand appropriately, excitation energy of f-f transition can be carried out wavelength 394 and near 420 or 465nm (all are blue), and the trivalent ion Eu³⁺ can carry out radiant energy near the wavelength of 600–700nm (red light). Among these, especially the excitation in the wavelength of 394nm has high luminous efficiency.

[0025] Moreover, it is the element of the atomic number 65 with which Tb similarly belongs to a lanthanoids, and the trivalent ion Tb³⁺ has the excitation energy of f-f transition near the wavelength of 300–380nm (all are blue), and the excitation especially in 380nm has the highest luminous efficiency. Moreover, luminescence by it is 488nm, 543nm, 581nm, 618nm, 652 etc.nm, etc., among these its 543nm (green light) luminescence intensity ratio excels and is strong.

[0026] It is the element of the atomic number 69 with which Tm similarly belongs to a lanthanoids, and the excitation wavelength of the trivalent ion Tm³⁺ is 400nm or less, and has excitation wavelength in 362nm in f-f transition. Luminescence of Tm is the strongest in the wavelength of 453nm (blue glow).

[0027] In addition, when the value (for example, "394nm") of specific wavelength is mentioned in this description, naturally before and after the value, the physical property or the width of face according to a measurement technique exists. For example, when the wavelength points out the wavelength of the excitation light of a rare earth complex, the width of face is not physicochemically based on the class of ligand, but it is a narrow thing 1nm or less approximately, but when a measurement technique etc. is taken into consideration, width of face of about several nm is included. Moreover, since bleedoff of much transition between level may be physicochemically included about the wavelength of firefly luminescence, the width of face may amount to 10nm or more.

[0028] As shown in drawing 3, the color coordinate on the chromaticity diagram of red luminescence of the above-mentioned complex (the 1st complex) which sets central ion to Eu is abbreviation (0.666 0.333), and the color coordinate of the complex (the 2nd complex) which sets central ion to Tb is abbreviation (0.313 0.631). And the color coordinate of those excitation blue glow is abbreviation (0.147 0.064). Since these three points are located on a chromaticity diagram at the top-most vertices of about 3 primary color RGB, the luminescence equipment which emits not only the white light of the color temperature of arbitration with high color rendering properties but also the light of the color of arbitration is realizable by mixing the 1st complex and the 2nd complex in transparency fixed support (a polymer, glass, etc.) by the ratio suitably, and combining them, and the blue light emitting diode or the semiconductor laser which is the excitation light source.

[0029] Moreover, when transparency fixed support is made to contain the 3rd complex which uses Tm as central ion, by combining with LED of near-ultraviolet region luminescence, or semiconductor laser, light can be emitted in RGB only with a complex and the luminescence equipment which emits light in the whiteness of the color temperature of arbitration or the color of arbitration can be realized similarly.

[0030] The spectrum when putting the sample which made the 1st complex of the above and the 2nd complex mix by the ratio suitably into polymer plastic on InGaN-LED which emits light in the blue of 440nm, and forming an emitter in drawing 4 is shown. RGB luminescence from each class was mixed and pink or the color tone of the pastel tone near the cut white is realized for a while.

[0031] In addition, two sorts or three sorts of complexes may not be mixed in transparency fixed support together, but these may be mixed in separate transparency fixed support, respectively, the laminating of all the transparency fixed support may be carried out, and luminescence equipment may be constituted by placing before the excitation light source. In this case, the luminescent color can be set as arbitration by adjusting suitably the concentration of the complex in each class (each transparency fixed support), or the thickness of each class.

[0032] By adjusting each above-mentioned complex concentration or the thickness of each class, the white of the color temperature of arbitration, for example, the source of the white light (the fluorescent lamp light source — for example) of color temperatures 6500K (daylight color), 5000K (daytime — white), 4200K (white), 3500K (** — white), and 3000K (electric bulb color) it realizes as cool [the object for study rooms] of PARUKKU (trademark of Matsushita Electric Industrial Co., Ltd.), natural [a Japanese-style room and the object for study rooms], and warm [living and the object for dining rooms] — **** — LED will also be realized. Since the fluorescence effectiveness of the complex to be used is as high as 40% – 70%, the point that luminous efficiency higher than the conventional technique is realizable also by the white light of a low color temperature is the big point.

[0033] Each transparency fixed support is made to contain simultaneously the sensitizing dye which can excite each central ion (Eu and Tb) selectively in the case of which, and you may make it control the luminescent color by that cause.

[0034] As the mixing approach to the fixed support of a complex, after mean particle diameter makes the host-guest complex of nano size support beforehand these complexes besides the approach of mixing in direct fixed support as mentioned above, the approach of making it mix in transparency fixed support may be used. In addition, the class and the manufacture approach of nano size host-guest complex of having made the rare earth complex supporting are indicated by the JP,2000-256251,A official report at the detail.

[0035] The light emitting diode or the semiconductor laser which has the nitride luminous layer expressed with general formula $In_xGa_{1-x}N$ ($0 < x < 1$) as the excitation light source for considering as white or arbitration color luminescence equipment combining the optical functional material concerning this invention is desirable. Although Semi-conductor LED or the semiconductor laser which has this luminous layer can make the light of the wavelength of the arbitration of blue – an ultraviolet area emit by controlling that component variable x, when Eu complex is used as a rare earth complex, the component variable x for generating the excitation light that wavelength 394 and near 420 or 465nm becomes 0.1 to about 0.5. Moreover, when Tb complex is used, the component variable x for generating the excitation light near the wavelength of 360–380nm becomes zero to about 0.1.

[Effect of the Invention]

[0036] Since the luminescence equipment concerning this invention is not what juxtaposed three separate sources of colored light, even if it sees finely, each color does not look separately and it serves as a completely homogeneous source of the white light. Moreover, the problem of an interference fringe does not arise at the time of photography etc. Furthermore, since the reinforcement of RGB each color is being fixed by concentration, layer thickness, etc. of each complex, there is almost no aging, and the source of the white light stabilized in the long run is obtained. And since luminescence equipment is only transparency fixed support arranged in the light source and its front face, it can use equipment itself as a compact dramatically.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the luminescence equipment which combined the optical functional material which consists of the wavelength conversion matter containing the organic fluorescent substance which consists of a rare earth complex, and the light emitting diode or the semiconductor laser which excites this organic fluorescent substance. The luminescence equipment concerning this invention can use the high source of the white light or arbitration color of color rendering properties as luminescence equipment which can emit light.

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PRIOR ART

[Description of the Prior Art] One of the descriptions of light emitting diode (LED) is a thing with high (that is, the spectrum full width at half maximum is narrow) monochromaticity. The full color display which carried out array mounting of the LED emitter which consists of a (Red R) green (G) blue (B) color in all directions on the flat surface is already widely used using this description. In this case, the foreground color is controlled by the intensity ratio of RGB each color to arbitration.

[0003] However, when it sees not as a display but as a lighting system, many problems are still left behind to LED. As mentioned above, although the white light can also be acquired by using the equipment which arranged the LED emitter of RGB and setting up the intensity ratio of RGB each color suitably When it sees as a lighting system, as compared with the incandescent lamp and fluorescent lamp which are the conventional lighting system, there are problems, like that (1) (3) which must control independently (2) RGB each color by which mixture in three primary colors will be checked by looking if it sees finely equipment becomes large-scale, and (4 "color rendering properties") is bad.

[0004] "Color rendering properties" means the property of the light source whether a body is visible to what kind of color here, when a body is illuminated by the light source. In view of the importance of the color rendering properties in a lighting system, CIE (Commission Internationale de l'Eclairage, Commission Internationale de l'Eclairage) defined the color-rendering-properties assessment approach in 1964. According to this, the series of the criteria light source which can be chosen with the color temperature of the light source for assessment is defined, and a color rendering index Ra is defined from the color gap when illuminating a regular trial color by the criteria light source and the light source for assessment. A color rendering index Ra takes the value of 0-100, and the light source's for assessment corresponds with the criteria light source in how whose color is visible at the time of 100. As the criteria light source, color temperature 5000K or less, when exceeding 5000K for a full radiator, the calculated value (it is called the synthetic daylight) of the spectral distribution of the daylight is used. Eight colors which have a predetermined spectral reflectance as an object for general as a trial color are chosen, and the color rendering index calculated by this is called a general color rendering index. In addition, seven colors are chosen as an object for the special objects, and Japanese flesh color is contained in it. The color rendering index calculated by this is called a special color rendering index. Furthermore, please refer to "illuminating engineering" for details (from the edited by Institute of Electrical Engineers of Japan, the Ohm-Sha **, and p.36).

[0005] It is based on the light of a full radiator in the case of color-rendering-properties assessment because the natural light (sunlight) is close to the light of a full radiator. The light of each wavelength is continuously contained in the light which a full radiator emits. Since the hue of an object is determined by the rate of a light reflex for every wavelength of an object (spectral reflectance), if the intensity distribution are [that the light of each wavelength is contained continuously] close to it of a full radiator in the spectral distribution of the illumination light (emitter), how whose color of an object is visible will become a thing near it under the natural light. However, even if the LED white emitter constituted from RGB makes the white light emit light as the whole by adjusting the intensity ratio of each color even if, the spectral distribution are discontinuous things which have the peak of narrow width of face only in three waves of parts, R (red), G (green), and B (blue), rather than are continuous. Because of this discontinuity, a RGB-LED emitter cannot have color rendering properties sufficient as a lighting system.

[0006] As the light source for white lighting using single LED, what (or it applied) covered current and gallium nitride system blue LED with the YAG fluorescent substance is devised (refer to JP,5-152609,A official report). This carries out optical pumping of the YAG fluorescent substance using the blue glow (wavelength of 460nm) from the InGaN barrier layer of gallium nitride system blue LED, and acquires the white light with the color mixture of the yellow luminescence and the blue from LED which are the fluorescence from the fluorescent substance.

[0007] The spectrum of white LED (correlated color temperature: 6500K) which consists of gallium nitride system blue LED which applied the YAG fluorescent substance to drawing 1, and the spectrum of the standard light D65 (correlated color temperature: 6504K) are shown. The standard light D65 is the standard light for color rendering assessment representing the daylight of color temperature 6504K here, and it is set by CIE by statistics processing of the actual measurement of natural daylight spectral distribution. As compared with the standard light D65 for color rendering assessment, as for the spectrum distribution of white LED, the spectrum distribution of a purple - purple-blue field, a bluish green - green field, and a red field is low. Although the color rendering index of white LED is shown in drawing 2, corresponding to spectrum distribution, it turns out are purple-blue and that the special color rendering index of green and red is inferior. therefore, the field to apply — it is necessary to reinforce the spectrum component needed with a certain form, and to raise the color rendering properties of an object

[0008] On the other hand, also in the white LED technique by the blue and the YAG fluorescent substance of the conventional technique, a color temperature is controllable by the increase of coverage, or carrying out and changing of a YAG fluorescent substance] the luminescence component (the amount of illuminants) from a fluorescent substance (refer to drawing 5). However, when the color temperature used with the sufficient actual condition makes the luminescence component from [from, the 6500K neighborhood] a fluorescent substance increase and makes a color temperature low, the following two troubles exist.

- (1) Since the fluorescence effectiveness of a YAG fluorescent substance is about 20%, the more it strengthens the luminescence component from a YAG fluorescent substance, the more the luminous efficiency as white LED will fall.
- (2) since a YAG fluorescent substance has the weak color component with it, yellowness is strong and its red color rendering properties are bad — unnatural — it will be white. [a strong yellow component and] [red]

[0009] A medical applicable field is described as an example. In the sea hospital in September 11, 2000 and Kyoto

prefectural Yosa, the first surgical operation (internal shunt construction way to a chronic-renal-failure patient) was performed, and it succeeded in the world using a white LED lighting system. This lighting system arranges in the shape of an array, the white LED chip which consists of gallium nitride system blue LED which applied the YAG fluorescent substance, uses it as an illuminant panel, and this is mounted in plastics goggles and it produces it. This operation was conducted by obtaining sufficient illuminance under dc-battery actuation, and the usefulness of white LED is proved [operation] as a handy lighting device which a surgeon can carry.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention]

[0036] Since the luminescence equipment concerning this invention is not what juxtaposed three separate sources of colored light, even if it sees finely, each color does not look separately and it serves as a completely homogeneous source of the white light. Moreover, the problem of an interference fringe does not arise at the time of photography etc. Furthermore, since the reinforcement of RGB each color is being fixed by concentration, layer thickness, etc. of each complex, there is almost no aging, and the source of the white light stabilized in the long run is obtained. And since luminescence equipment is only transparency fixed support arranged in the light source and its front face, it can use equipment itself as a compact dramatically.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, it was pointed out about the color rendering properties of white LED at the time of the above-mentioned operation that it is hard to recognize the blood vessel (blackish red) of an artery (clear red) and a vein. This is because a problem is in the color rendering properties in the red field of used white LED, and is considered that the reddish spectrum of orange or a 640–780nm red field which is 597–640nm is solvable by strengthening.

[0011] As a means which strengthens the spectrum of a red field, distributing the AlGaInP system LED or the AlGaAs system LED in all directions on a flat surface in a white LED chip is considered first. However, in order to mix an emission spectrum uniformly within a radial plane, it will be necessary to distribute mounting of a chip uniformly as densely as possible, or to mount a diffusion plate in an LED emitter panel front face. And the reinforcement of white LED (YAG fluorescent substance spreading=gallium nitride system blue LED) and red LED (the AlGaInP system LED or the AlGaAs system LED) must be controlled independently.

[0012] The easiest approach of strengthening the spectrum of a red field, without producing the above-mentioned problem is applying to the present white LED the fluorescent substance which emits light in a red field. However, when aimed at the lighting system generally used widely, moreover as the red fluorescent substance, it becomes indispensable requirements with a well head that it is extremely stable. And the point that workability is high, and the points which do not contain matter which pollutes earth environment even if abandoned excluding a poisonous component to the body are also important requirements.

[0013] As a fluorescent substance of a red field, if organic molecule ingredients, such as a rhodamine, are used, high luminous efficiency will be acquired, but since decomposition and **** arise easily by optical exposure, it is not suitable for practical use. The ZnCdS:Ag system and the Y2O2 S:Eu³⁺ system fluorescent substance are used as a Braun-tube red fluorescent substance (electron beam pumping) of television, and comparatively high red conversion is obtained by the LED light source (360–380nm) of an ultraviolet area. However, since conversion efficiency sufficient in blue excitation is not acquired, it is uncombinable with white LED (YAG fluorescent substance spreading=gallium nitride system blue LED) used now. If the present luminous efficiency ultraviolet [LED] is markedly alike as compared with blue LED and considers a low point, the combination with this practical will not become. And long term stability is obtained only within the Braun tube stopped by the vacuum, in the environment in atmospheric air, moisture absorption arises, photochemical reaction is accelerated and the problem that degradation of a fluorescent substance occurs produces these fluorescent substances. The closure technique for solving this is not yet developed. Furthermore, the ZnCdS:Ag system contains Cd and it is apprehensive about the effect on an environment.

[0014] Considering such a thing, about the red fluorescent substance in which the present white LED and combination are possible, the fluorescent substance developed so far has various problems.

[0015] Fluorescence ingredients various by adding rare earth metals, such as Eu (europium), Tb (terbium), and Tm (thulium), in matter, such as an inorganic oxide and inorganic sulfide, conventionally have been developed. However, conventionally, "A rare earth metal could not emit light easily in an organic medium" was presupposed, and the luminous efficiency of the rare earth metal in the inside of organic media, such as a plastics system, was actually dramatically lower than the energy gap theory of quantum physics till recent years.

[0016] On the other hand, the thing for which some these artificers are begun from re-evaluation of the energy gap theory — a group of rare earth metals, such as neodymium which can emit light in an organic medium for the first time in the world in 1995, — it succeeded in the design of a complex (the Hasegawa ****, "how the neodium which does not shine in an organic medium to be shone", chemistry, industry, volume [53rd] (2000) No. 2, and pp.126–130). Patent application was also performed about these parts (PCT/JP98/00970=WO98/40388 official report, a Japanese-Patent-Application-No. 10-238973= JP,2000-63682,A official report, Japanese-Patent-Application-No. 11-62298= JP,2000-256251,A official report).

[0017] These complexes are stable also in the elevated temperature of 350 degrees C, it is hard to produce photodegradation, and an organic compound reverses the conventional common sense of being easy to produce degradation by heat or optical exposure. Moreover, compatibility with the host ingredient of a resin system called plastics and a polymer is also high, and becoming easy workability with a next-generation light corpuscle child conjointly is expected.

[0018] First of all, this invention realizes the high white luminescence equipment of color rendering properties by choosing and using the matter suitable for especially the object in these complexes. Moreover, it is also possible for this invention not to stop at mere white luminescence equipment, but to use light of an arbitration color as the equipment which emits light.

[Translation done.]

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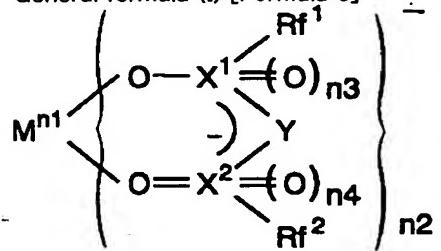
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MEANS

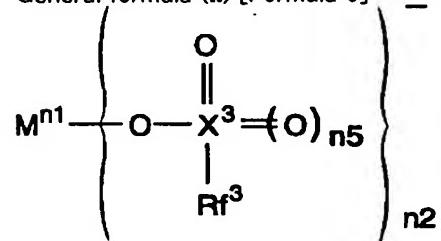
[Means for Solving the Problem] The optical high-performance material concerning this invention accomplished in order to solve the above-mentioned technical problem has the structure expression of either the following general formula (I) - (VII), and is characterized by consisting of the transparency solid support containing the 1st complex whose central ion M is Eu (europium), and the 2nd complex whose central ion M it has the structure expression of either a general formula (I) - (VII) similarly, and is Tb (terbium).

General formula (I) [Formula 8]



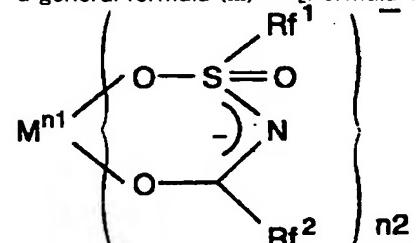
(In this formula, n₁ shows 2 or 3.) n₂ shows 2, 3, or 4. Rf₁ and Rf₂ show the same or the heterocycle radical which does not contain the different aromatic series radical or different hydrogen atom which does not contain the aliphatic series radical of C1-C22 which do not contain a hydrogen atom, and a hydrogen atom. X₁ and X₂ show either the same, or a different IVA group atom, VA group atom except nitrogen and the VIA group atom except oxygen. n₃ and n₄ show 0 or 1. Y shows C-Z' (Z' shows the aliphatic series radical of C1-C22 which do not contain heavy hydrogen, a halogen atom, or a hydrogen atom), N, P, As and Sb, or Bi. However, when X₁ is a carbon atom, n₃ is 0, when X₂ is a carbon atom, n₄ is 0 and, in the case of a carbon atom, X₁ and X₂ are the aromatic series radicals in which at least one side of Rf₁ and Rf₂ does not contain a hydrogen atom simultaneously.

General formula (II) [Formula 9]



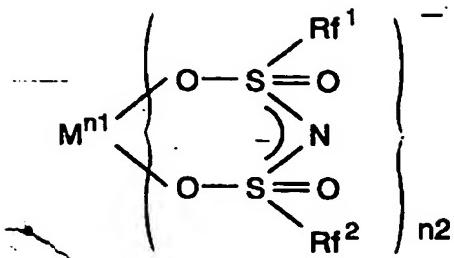
(In this formula, n₁ and n₂ are as aforementioned.) Rf₃ shows the heterocycle radical which does not contain the aromatic series radical or hydrogen atom which does not contain the aliphatic series radical of C1-C22 which do not contain a hydrogen atom, and a hydrogen atom. X₃ shows the IVA group atom except carbon, VA group atom except nitrogen, or the VIA group atom except oxygen. n₅ shows 0 or 1.

a general formula (III) -- [Formula 10]

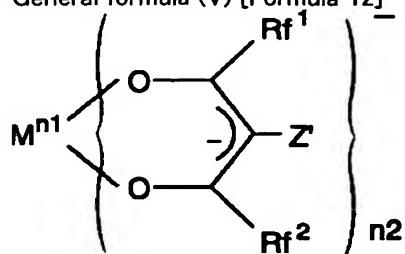


(In this formula, Rf₁, Rf₂, n₁, and n₂ are as aforementioned.)

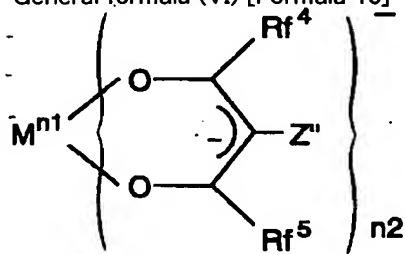
General formula (IV) [Formula 11]



(In this formula, Rf^1 , Rf^2 , n_1 , and n_2 are as aforementioned.)
General formula (V) [Formula 12]

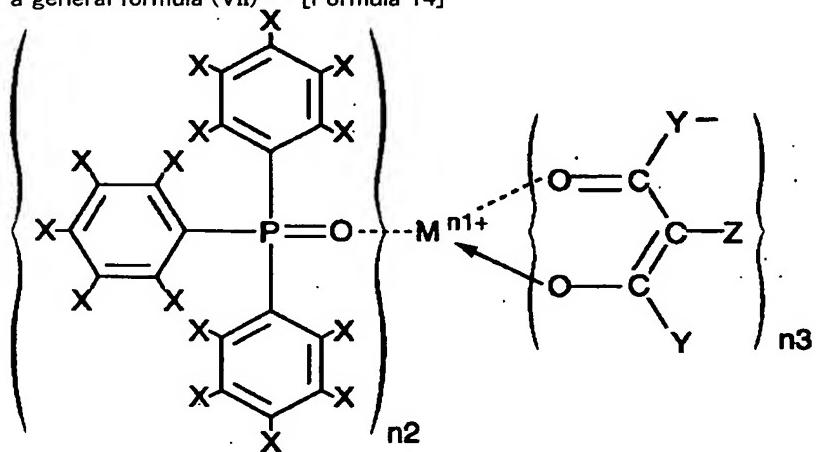


(In this formula, Rf^1 , Rf^2 , n_1 , n_2 , and Z' are as aforementioned.)
General formula (VI) [Formula 13]



(In this formula, n_1 and n_2 are as aforementioned.) Z'' shows a hydrogen atom or Z' (Z' is the same as the above). Rf^4 and Rf^5 show the same or the heterocycle radical which does not contain the different aromatic series radical or different hydrogen atom which does not contain the aliphatic series radical of C1-C22 which do not contain a hydrogen atom, and a hydrogen atom.

a general formula (VII) — [Formula 14]



(In this formula, n_1 shows 2 or 3.) n_2 shows 1 or 2. n_3 shows 1, 2, 3, or 4. X shows the same or a different hydrogen atom, a heavy hydrogen atom, a halogen atom, the radical of C1-C20, a hydroxyl group, a nitro group, the amino group, a sulfonyl group, a cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulphydryl group. Y shows the same or a different radical of C1-C20, a hydroxyl group, a nitro group, the amino group, a sulfonyl group, cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulphydryl group. Z shows a hydrogen atom or a heavy hydrogen atom.

[0020] In addition, in addition to these 1st complexes and the 2nd complex, it has the structure expression of either the same general formula (I) – (VII), and the 3rd complex whose central ion M is Tm (thulium) may be added. When this 3rd complex is added, the light source of a near-ultraviolet region is used as the excitation light source, and the 1st – the 3rd complex are made to emit light simultaneously.

[0021] General formula (I) Since the aliphatic series radical of C1-C22 which do not contain the hydrogen atom of – (VI), the aromatic series radical which does not contain a hydrogen atom, the heterocycle radical which does not contain a hydrogen atom, and the example of X1, X2, and X3 are indicated by [0031] – [0037] of a JP,2000-63682,A official report, refer for them there to. Moreover, the synthesis method of the above-mentioned complex is also

indicated by [0047] – [0067] of this official report.

[0022] In addition, in these rare earth complexes, Rf1 and Rf2 are good in respect of compatibility with plastics and the polymer whose thing_to_C1_or_about two C is the below-mentioned transparency solid support, and they generate a polymer with stable CF3 or CF2CF3 especially also in it.

[0023] Also about the complex expressed with a general formula (VII), the detail is indicated by [0012] – [0021] of an application for patent 2001-272547, and the synthesis method is indicated by [0024] – [0027].

[0024]

[Embodyment of the Invention] Eu is the element of the atomic number 63 belonging to a lanthanoids, by designing a ligand appropriately, excitation energy of f-f transition can be carried out wavelength 394 and near 420 or 465nm (all are blue), and the trivalent ion Eu³⁺ can carry out radiant energy near the wavelength of 600–700nm (red light). Among these, especially the excitation in the wavelength of 394nm has high luminous efficiency.

[0025] Moreover, it is the element of the atomic number 65 with which Tb similarly belongs to a lanthanoids, and the trivalent ion Tb³⁺ has the excitation energy of f-f transition near the wavelength of 300–380nm (all are blue), and the excitation especially in 380nm has the highest luminous efficiency. Moreover, luminescence by it is 488nm, 543nm, 581nm, 618nm, 652 etc.nm, etc., among these its 543nm (green light) luminescence intensity ratio excels and is strong.

[0026] It is the element of the atomic number 69 with which Tm similarly belongs to a lanthanoids, and the excitation wavelength of the trivalent ion Tm³⁺ is 400nm or less, and has excitation wavelength in 362nm in f-f transition. Luminescence of Tm is the strongest in the wavelength of 453nm (blue glow).

[0027] In addition, when the value (for example, "394nm") of specific wavelength is mentioned in this description, naturally before and after the value, the physical property or the width of face according to a measurement technique exists. For example, when the wavelength points out the wavelength of the excitation light of a rare earth complex, the width of face is not physicochemically based on the class of ligand, but it is a narrow thing 1nm or less approximately, but when a measurement technique etc. is taken into consideration, width of face of about several nm is included. Moreover, since bleedoff of much transition between level may be physicochemically included about the wavelength of firefly luminescence, the width of face may amount to 10nm or more.

[0028] As shown in drawing 3, the color coordinate on the chromaticity diagram of red luminescence of the above-mentioned complex (the 1st complex) which sets central ion to Eu is abbreviation (0.666 0.333), and the color coordinate of the complex (the 2nd complex) which sets central ion to Tb is abbreviation (0.313 0.631). And the color coordinate of those excitation blue glow is abbreviation (0.147 0.064). Since these three points are located on a chromaticity diagram at the top-most vertices of about 3 primary color RGB, the luminescence equipment which emits not only the white light of the color temperature of arbitration with high color rendering properties but also the light of the color of arbitration is realizable by mixing the 1st complex and the 2nd complex in transparency fixed support (a polymer, glass, etc.) by the ratio suitably, and combining them, and the blue light emitting diode or the semiconductor laser which is the excitation light source.

[0029] Moreover, when transparency fixed support is made to contain the 3rd complex which uses Tm as central ion, by combining with LED of near-ultraviolet region luminescence, or semiconductor laser, light can be emitted in RGB only with a complex and the luminescence equipment which emits light in the whiteness of the color temperature of arbitration or the color of arbitration can be realized similarly.

[0030] The spectrum when putting the sample which made the 1st complex of the above and the 2nd complex mix by the ratio suitably into polymer plastic on InGaN-LED which emits light in the blue of 440nm, and forming an emitter in drawing 4 is shown. RGB luminescence from each class was mixed and pink or the color tone of the pastel tone near the cut white is realized for a while.

[0031] In addition, two sorts or three sorts of complexes may not be mixed in transparency fixed support together, but these may be mixed in separate transparency fixed support, respectively, the laminating of all the transparency fixed support may be carried out, and luminescence equipment may be constituted by placing before the excitation light source. In this case, the luminescent color can be set as arbitration by adjusting suitably the concentration of the complex in each class (each transparency fixed support), or the thickness of each class.

[0032] By adjusting each above-mentioned complex concentration or the thickness of each class, the white of the color temperature of arbitration, for example, the source of the white light (the fluorescent lamp light source — for example) of color temperatures 6500K (daylight color), 5000K (daytime — white), 4200K (white), 3500K (** — white), and 3000K (electric bulb color) it realizes as cool [the object for study rooms] of PARUKKU (trademark of Matsushita Electric Industrial Co., Ltd.), natural [a Japanese-style room and the object for study rooms], and warm [living and the object for dining rooms] — **** — LED will also be realized. Since the fluorescence effectiveness of the complex to be used is as high as 40% – 70%, the point that luminous efficiency higher than the conventional technique is realizable also by the white light of a low color temperature is the big point.

[0033] Each transparency fixed support is made to contain simultaneously the sensitizing dye which can excite each central ion (Eu and Tb) selectively in the case of which, and you may make it control the luminescent color by that cause.

[0034] As the mixing approach to the fixed support of a complex, after mean particle diameter makes the host-guest complex of nano size support beforehand these complexes besides the approach of mixing in direct fixed support as mentioned above, the approach of making it mix in transparency fixed support may be used. In addition, the class and the manufacture approach of nano size host-guest complex of having made the rare earth complex supporting are indicated by the JP.2000-256251,A official report at the detail.

[0035] The light emitting diode or the semiconductor laser which has the nitride luminous layer expressed with general formula In_xGa_{1-x}N (0 < x < 1) as the excitation light source for considering as white or arbitration color luminescence equipment combining the optical functional material concerning this invention is desirable. Although Semi-conductor LED or the semiconductor laser which has this luminous layer can make the light of the wavelength of the arbitration of blue – an ultraviolet area emit by controlling that component variable x, when Eu complex is used as a rare earth complex, the component variable x for generating the excitation light that wavelength 394 and near 420 or 465nm becomes 0.1 to about 0.5. Moreover, when Tb complex is used, the component variable x for generating the excitation light near the wavelength of 360–380nm becomes zero to about 0.1.

[Translation done.]

*** NOTICES ***

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- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The graph of the spectrum of white LED (correlated color temperature: 6500K) which consists of gallium nitride system blue LED which applied the YAG fluorescent substance, and the spectrum of the standard light D65 (correlated color temperature: 6504K).

[Drawing 2] The table of the color rendering index of white LED and the other sources of the white light.

[Drawing 3] Chromaticity diagram.

[Drawing 4] Spectrum drawing when putting the sample which made the 1st complex and the 2nd complex mix by the ratio suitably into polymer plastic on the InGaN-LED light source, and forming an emitter in it.

[Drawing 5] The graph of the chromaticity coordinate which white LED of an InGaN system blue LED+YAG system fluorescent substance method covers, and correlated color temperature.

[Translation done.]

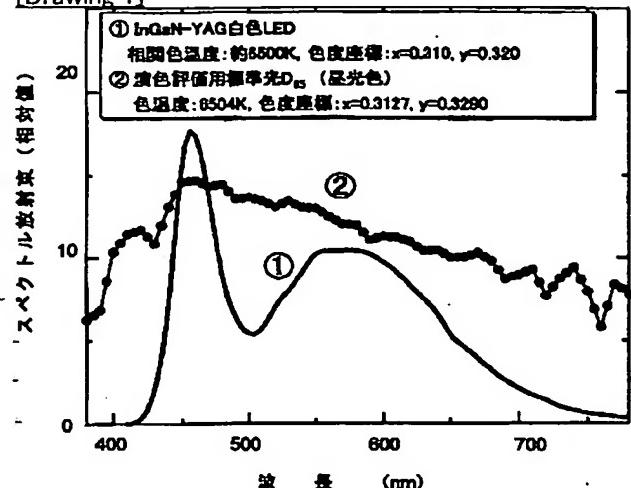
* NOTICES *

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- 3.In the drawings, any words are not translated.

DRAWINGS

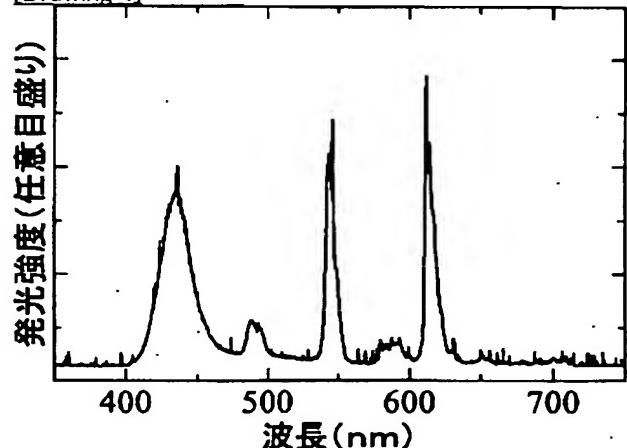
[Drawing 1]



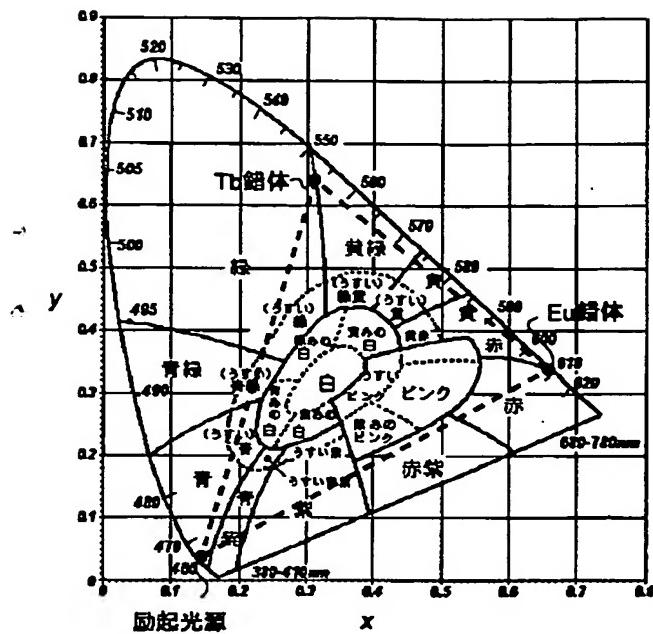
[Drawing 2]

ランプ種類	色度		平均演色評価数	特殊演色評価数						効率 [lm/W]		
	x	y		赤 R ₁	黄 R ₂	緑 R ₃	青紫 R ₄	蓝色 R ₅	木の葉 R ₆			
星光色 D	0.309	0.336	D6500	77	-52	63	63	78	73	98	58	73
白色 W	0.360	0.366	P6500	69	-76	58	51	61	65	95	60	86
天然白色 WDL	0.361	0.363	P4500	87	54	73	83	78	86	94	86	86
色評価用純正色 W-ECDL-50K	0.347	0.361	P6000	98	90	95	98	95	98	98	97	55
InGaN-YAG系白色LED	0.310	0.320	D6500	87	51	87	73	62	92	98	98	20

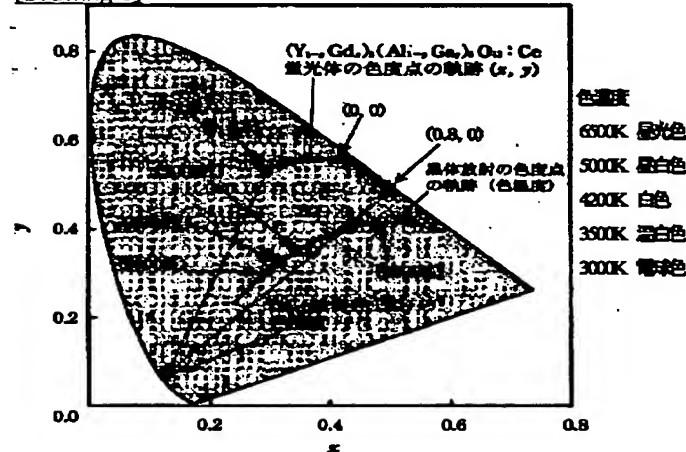
[Drawing 4]



[Drawing 3]



[Drawing 5]



[Translation done.]

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CORRECTION OR AMENDMENT

[Kind of official gazette] Printing of amendment by the convention of 2 of Article 17 of Patent Law
[Category partition] The 3rd partition of the 3rd category
[Publication date] March 17, Heisei 17 (2005. 3.17)

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[Date of Publication] May 21, Heisei 15 (2003. 5.21)
[Application number] Application for patent 2001-350723 (P2001-350723)
[The 7th edition of International Patent Classification]

C09K 11/06
H01L 33/00
H01S 5/00
H01S 5/323

-[FI]

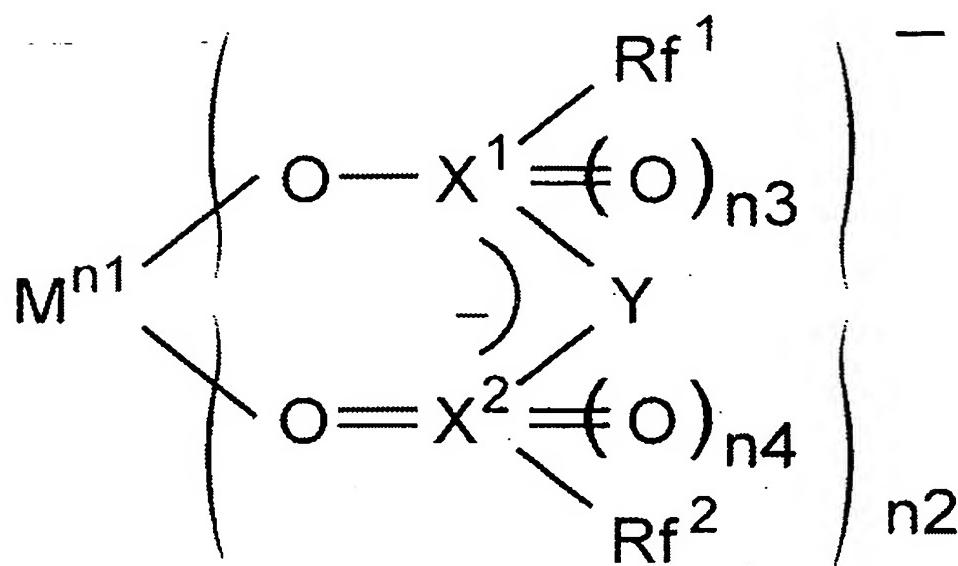
C09K 11/06 660
H01L 33/00 C
H01L 33/00 L
H01S 5/00
H01S 5/323 610

[Procedure amendment]
[Filing Date] April 15, Heisei 16 (2004. 4.15)
[Procedure amendment 1]
[Document to be Amended] Description
[Item(s) to be Amended] Claim
[Method of Amendment] Modification
[The content of amendment]
[Claim(s)]
[Claim 1]

The optical functional material which has the structure expression of either a general formula (I) – (VII), and consists of the transparency fixed support which contains the 1st complex whose central ion M is Eu, and the 2nd complex whose central ion M it has the structure expression of either a general formula (I) – (VII) similarly, and is Tb together.

General formula (I)

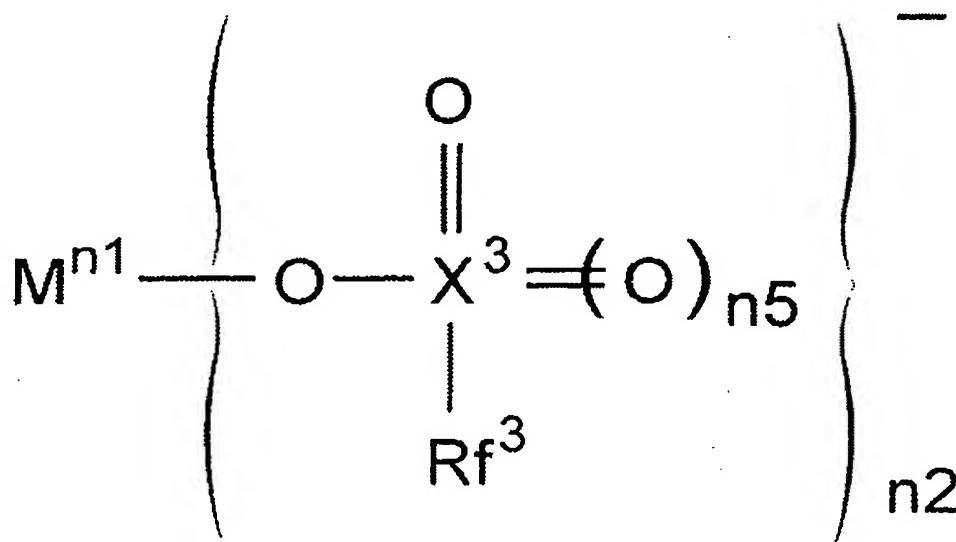
[Formula 1]



(In this formula, n1 shows 2 or 3.) n2 shows 2, 3, or 4. Rf1 and Rf2 show the same or the heterocycle radical which does not contain the different aromatic series radical or different hydrogen atom which does not contain the aliphatic series radical of C1-C22 which do not contain a hydrogen atom, and a hydrogen atom. X1 and X2 show either the same, or a different IVA group atom, VA group atom except nitrogen and the VIA group atom except oxygen, n3 and n4 show 0 or 1. Y shows C-Z' (Z' shows the aliphatic series radical of C1-C22 which do not contain heavy hydrogen, a halogen atom, or a hydrogen atom), N, P, As and Sb, or Bi. However, when X1 is a carbon atom, n3 is 0, when X2 is a carbon atom, n4 is 0 and, in the case of a carbon atom, X1 and X2 are the aromatic series radicals in which at least one side of Rf1 and Rf2 does not contain a hydrogen atom simultaneously.

General formula (II)

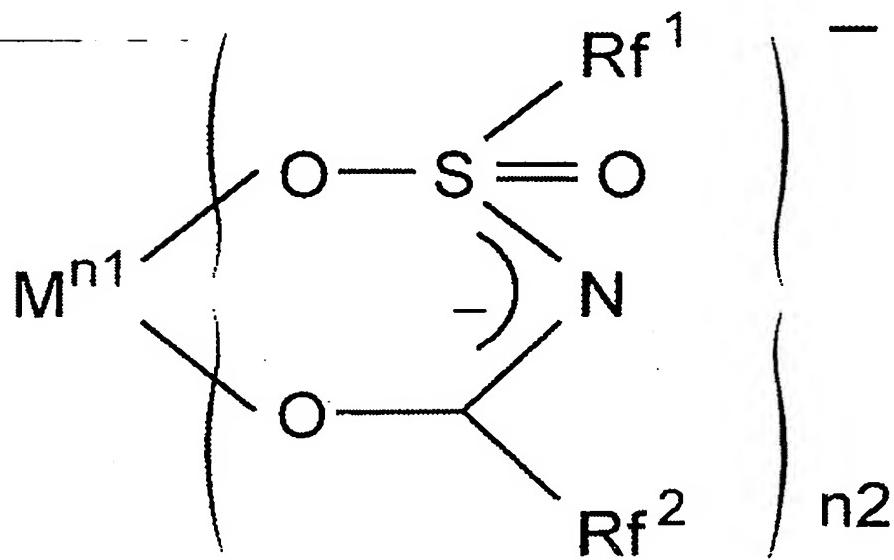
[Formula 2]



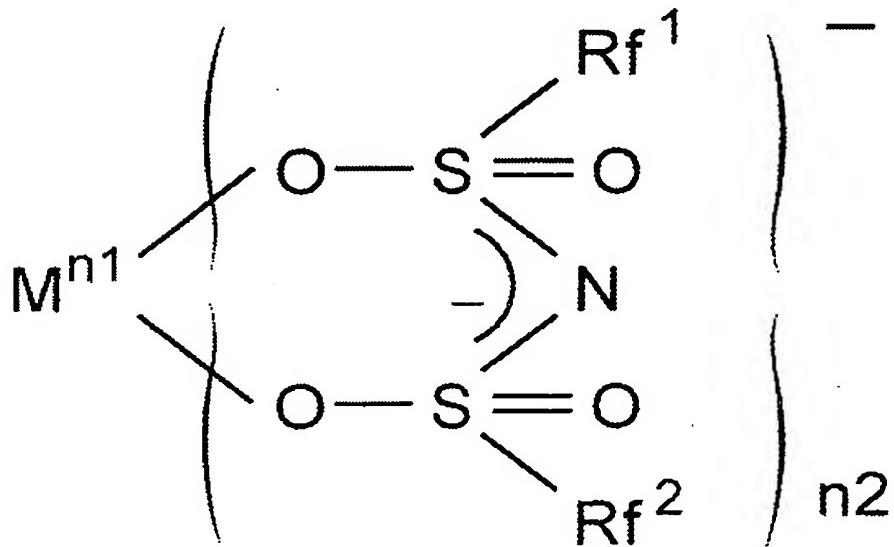
(In this formula, n1 and n2 are as aforementioned.) Rf3 shows the heterocycle radical which does not contain the aromatic series radical or hydrogen atom which does not contain the aliphatic series radical of C1-C22 which do not contain a hydrogen atom, and a hydrogen atom. X3 shows the IVA group atom except carbon, VA group atom except nitrogen, or the VIA group atom except oxygen. n5 shows 0 or 1.

General formula (III)

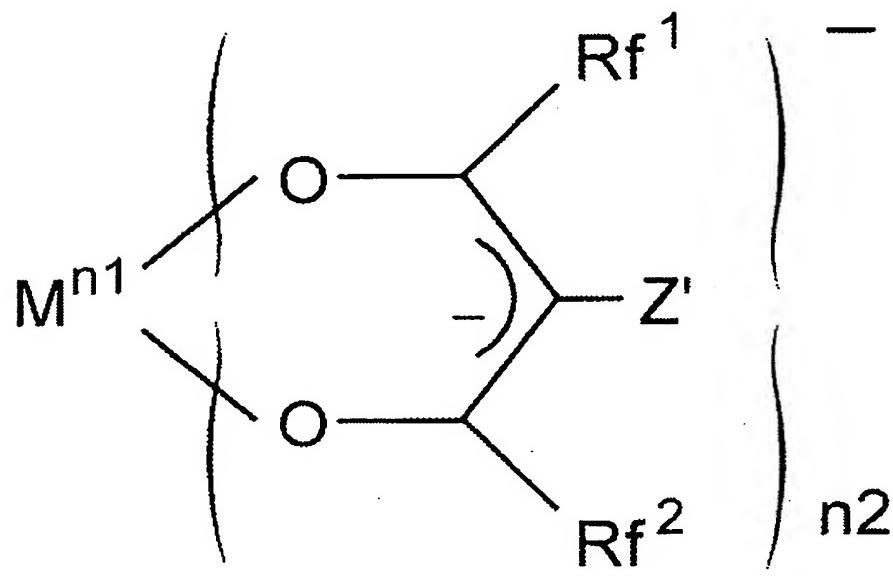
[Formula 3]



(In this formula, $\text{Rf}1$, $\text{Rf}2$, $n1$, and $n2$ are as aforementioned.)
General formula (IV)
[Formula 4]



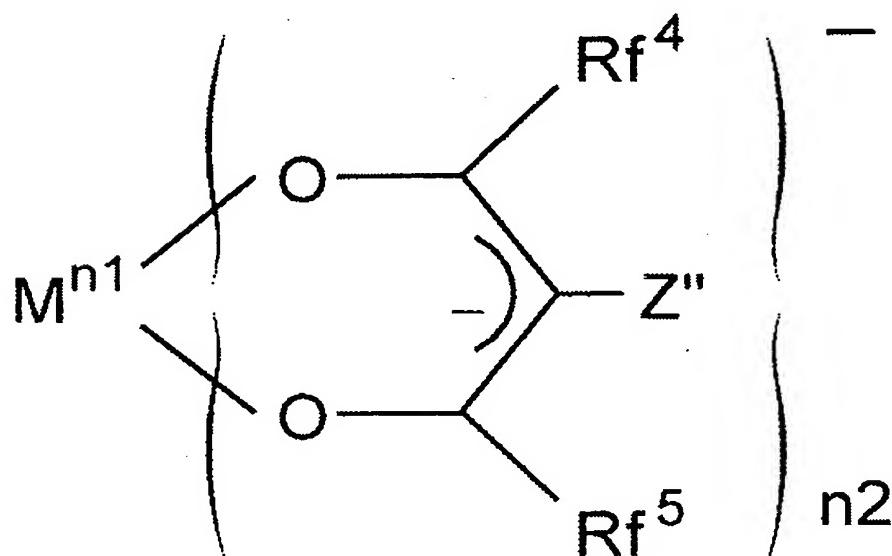
(In this formula, $\text{Rf}1$, $\text{Rf}2$, $n1$, and $n2$ are as aforementioned.)
General formula (V)
[Formula 5]



(In this formula, $Rf1$, $Rf2$, $n1$, $n2$, and Z' are as aforementioned.)

General formula (VI)

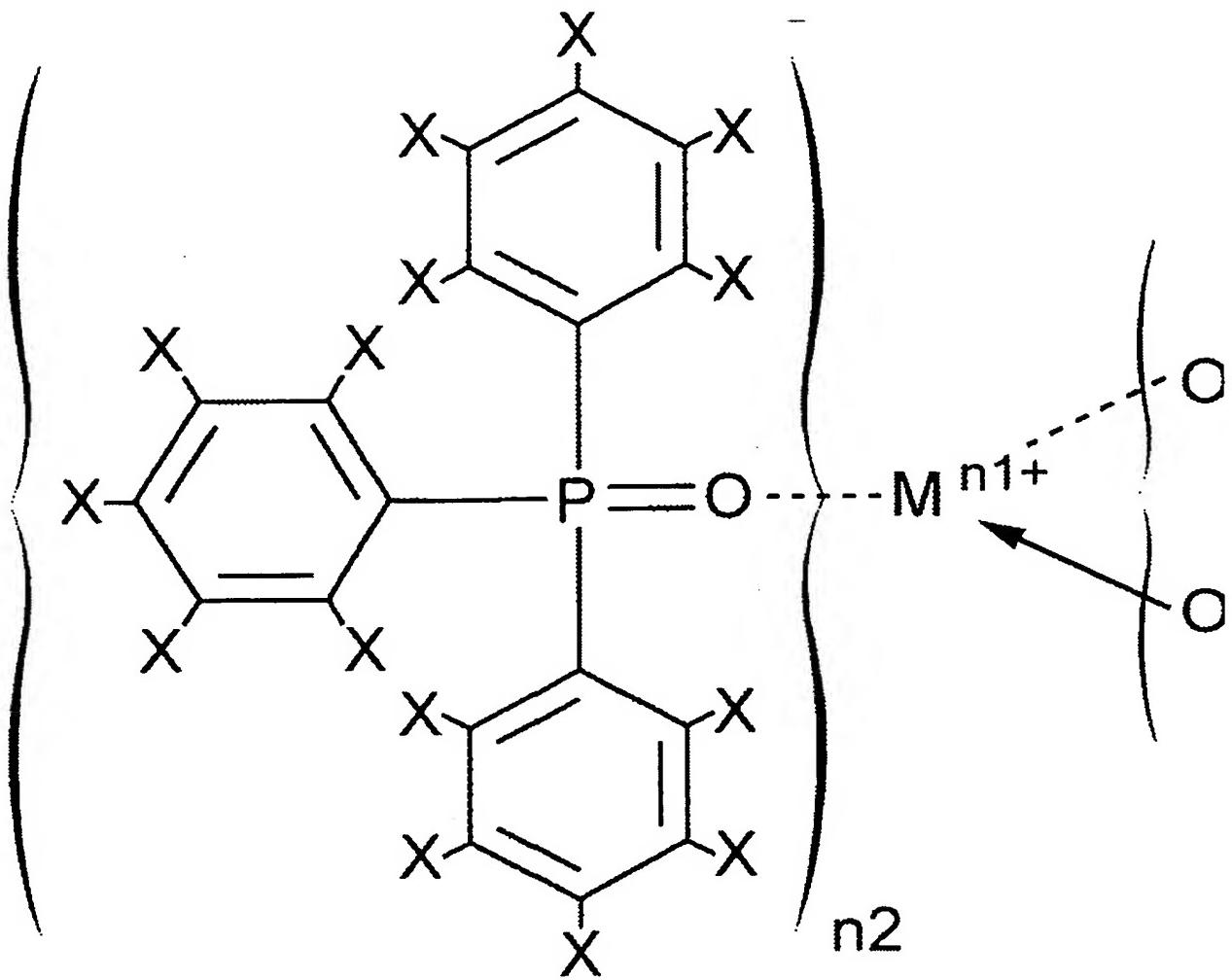
[Formula 6]



(In this formula, $n1$ and $n2$ are as aforementioned.) Z' shows a hydrogen atom or Z' (the aforementioned passage). $Rf4$ and $Rf5$ show the same or the heterocycle radical which does not contain the different aromatic series radical or different hydrogen atom which does not contain the aliphatic series radical of C1-C22 which do not contain a hydrogen atom, and a hydrogen atom.

General formula (VII)

[Formula 7]



(In this formula, n1 shows 2 or 3.) n2 shows 1 or 2. n3 shows 1, 2, 3, or 4. X shows the same or a different hydrogen atom, a heavy hydrogen atom, a halogen atom, the radical of C1-C20, a hydroxyl group, a nitro group, the amino group, a sulfonyl group, a cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulfhydryl group. Y shows the same or a different radical of C1-C20, a hydroxyl group, a nitro group, the amino group, a sulfonyl group, a cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulfhydryl group. Z shows a hydrogen atom or a heavy hydrogen atom.

[Claim 2]

The optical functional material which carried out the laminating of the transparency fixed support which has the structure expression of either a general formula (I) according to claim 1 - (VII), and contains the 1st complex whose central ion M is Eu, and the transparency fixed support which similarly has the structure expression of either a general formula (I) according to claim 1 - (VII), and contains the 2nd complex whose central ion M is Tb.

[Claim 3]

Furthermore, the optical functional material according to claim 1 with which the above-mentioned transparency fixed support has the structure expression of either a general formula (I) - (VII), and also contains the 3rd complex whose central ion M is Tm.

[Claim 4]

The optical functional material which is characterized by providing the following and which carried out the laminating of the transparency fixed support Transparency fixed support which has the structure expression of either a general formula (I) according to claim 1 - (VII), and contains the 1st complex whose central ion M is Eu Transparency fixed support which similarly has the structure expression of either a general formula (I) according to claim 1 - (VII), and contains the 2nd complex whose central ion M is Tb The 3rd complex whose central ion M it similarly has the structure expression of either a general formula (I) according to claim 1 - (VII), and is Tm

[Claim 5]

The optical functional material according to claim 3 or 4 characterized by using the light source of a near-ultraviolet region as the excitation light source.

[Claim 6]

Luminescence equipment characterized by combining an optical functional material according to claim 1 to 5, and the light emitting diode or the semiconductor laser which emits the excitation light corresponding to the excitation wavelength range of each above-mentioned central ion.

[Claim 7]

Luminescence equipment according to claim 6 characterized by the above-mentioned excitation light having the wavelength corresponding to f-f transition of each above-mentioned central ion.

[Claim 8]

So that the light which doubled luminescence of the 1st complex, luminescence of the 2nd complex, and luminescence of the above-mentioned excitation light source may become white So that the light which doubled luminescence of the 1st complex, luminescence of the 2nd complex, and luminescence of the 3rd complex may become white Or concentration of the 1st complex in transparency fixed support and concentration of the 2nd complex, Or luminescence equipment according to claim 6 or 7 characterized by adjusting the concentration of the 1st complex, the concentration of the 2nd complex, the concentration of the 3rd complex, or the thickness of each transparency fixed support layer.

[Claim 9]

Luminescence equipment according to claim 6 to 8 characterized by the above-mentioned light emitting diode or semiconductor laser having the luminous layer expressed with general formula $In_xGa_{1-x}N$ ($0 < x < 1$).

[Claim 10]

Luminescence equipment according to claim 6 to 9 characterized by the above-mentioned transparency fixed support being transparency resin.

[Claim 11]

Luminescence equipment according to claim 6 to 10 characterized by including the sensitizing dye with which the above-mentioned transparency fixed support can excite each above-mentioned central ion selectively.

[Claim 12]

Luminescence equipment according to claim 6 to 11 characterized by the mean particle diameter with which the above-mentioned transparency fixed support supported the above-mentioned complex containing the complex (host-guest) of nano size.

- [Procedure amendment 2]

- [Document to be Amended] Description

- [Item(s) to be Amended] 0007

- [Method of Amendment] Modification

- [The content of amendment]

[0007]

The spectrum of white LED (correlated color temperature: 6500K) which consists of gallium nitride system blue LED which applied the YAG fluorescent substance to drawing 1, and the spectrum of the standard light D65 (correlated color temperature: 6504K) are shown. The standard light D65 is the standard light for color rendering assessment representing the daylight of color temperature 6504K here, and it is set by CIE by statistics processing of the actual measurement of natural daylight spectral distribution. As compared with the standard light D65 for color rendering assessment, as for the spectrum distribution of white LED, the spectrum distribution of a purple - purple-blue field, a bluish green - green field, and a red field is low. Although the color rendering index of white LED is shown in drawing 2, corresponding to spectrum distribution, it turns out are purple-blue and that the special color rendering index of green and red is inferior. Therefore, it is necessary to reinforce the spectrum component needed by the field to apply with a certain form, and to raise the color rendering properties of an object.

[Procedure amendment 3]

- [Document to be Amended] Description

- [Item(s) to be Amended] 0008

- [Method of Amendment] Modification

- [The content of amendment]

[0008]

On the other hand, also in the white LED technique by blue LED and the YAG fluorescent substance of the conventional technique, a color temperature is controllable by the increase of coverage, or carrying out and changing of a YAG fluorescent substance] the luminescence component (the amount of illuminants) from a fluorescent substance (refer to drawing 5). However, when the color temperature used with the sufficient actual condition makes the luminescence component from [from the 6500K neighborhood] a fluorescent substance increase and makes a color temperature low, the following two troubles exist.

(1) Since the fluorescence effectiveness of a YAG fluorescent substance is about 20%, the more it strengthens the luminescence component from a YAG fluorescent substance, the more the luminous efficiency as white LED will fall.

(2) since a YAG fluorescent substance has the weak color component with it, yellowness is strong and its red color rendering properties are bad — unnatural — it will be white. [a strong yellow component and] [red]

[Procedure amendment 4]

- [Document to be Amended] Description

- [Item(s) to be Amended] 0019

- [Method of Amendment] Modification

- [The content of amendment]

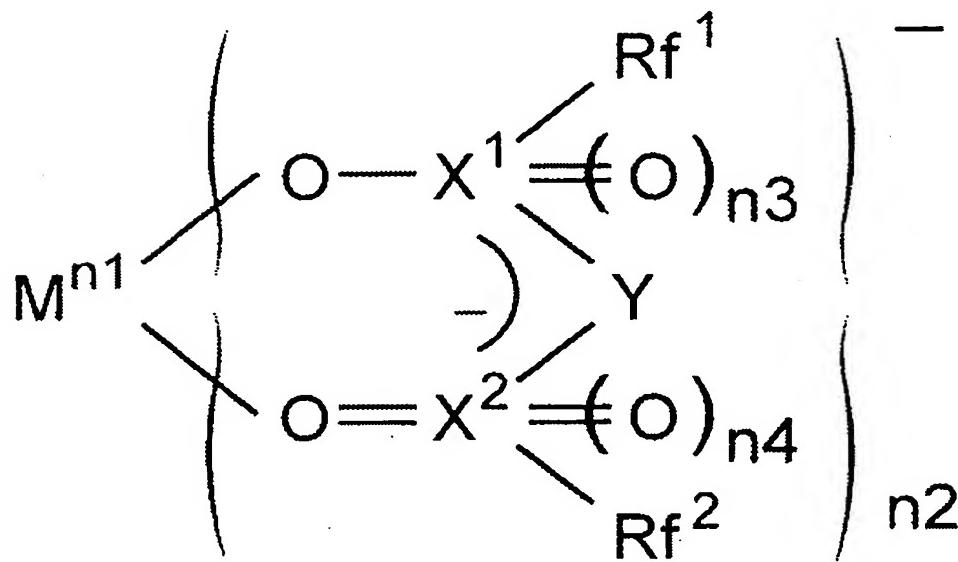
[0019]

[Means for Solving the Problem]

The optical high-performance material concerning this invention accomplished in order to solve the above-mentioned technical problem has the structure expression of either the following general formula (I) - (VII), and is characterized by consisting of the transparency fixed support containing the 1st complex whose central ion M is Eu (europium), and the 2nd complex whose central ion M it has the structure expression of either a general formula (I) - (VII) similarly, and is Tb (terbium).

General formula (I)

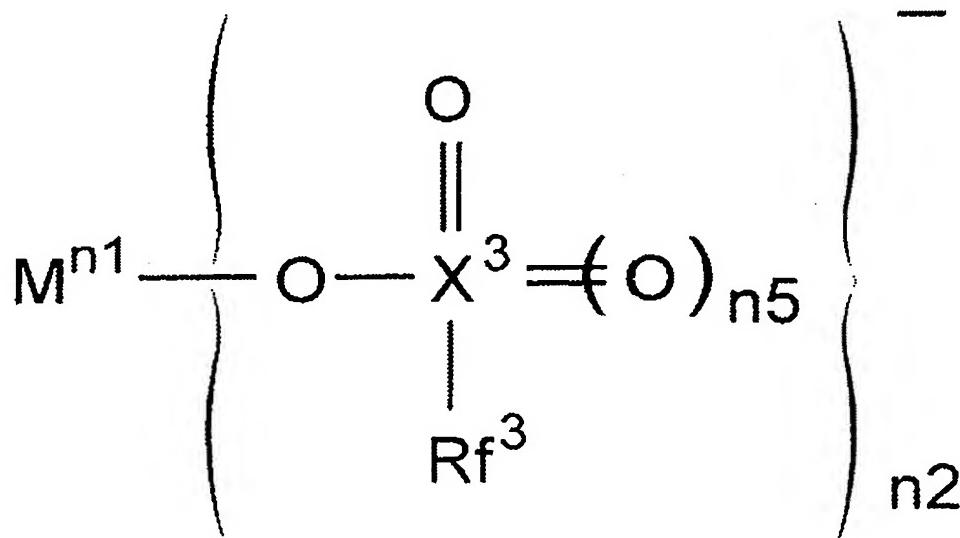
[Formula 8]



(In this formula, n1 shows 2 or 3.) n2 shows 2, 3, or 4. Rf1 and Rf2 show the same or the heterocycle radical which does not contain the different aromatic series radical or different hydrogen atom which does not contain the aliphatic series radical of C1-C22 which do not contain a hydrogen atom, and a hydrogen atom. X1 and X2 show either the same, or a different IVA group atom, VA group atom except nitrogen and the VIA group atom except oxygen, n3 and n4 show 0 or 1. Y shows C-Z' (Z' shows the aliphatic series radical of C1-C22 which do not contain heavy hydrogen, a halogen atom, or a hydrogen atom), N, P, As and Sb, or Bi. However, when X1 is a carbon atom, n3 is 0, when X2 is a carbon atom, n4 is 0 and, in the case of a carbon atom, X1 and X2 are the aromatic series radicals in which at least one side of Rf1 and Rf2 does not contain a hydrogen atom simultaneously.

General formula (II)

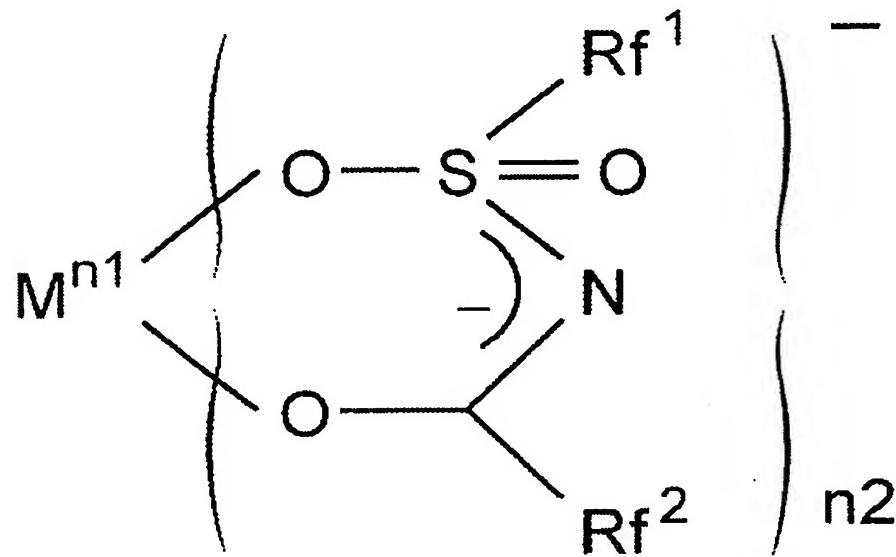
[Formula 9]



(In this formula, n1 and n2 are as aforementioned.) Rf3 shows the heterocycle radical which does not contain the aromatic series radical or hydrogen atom which does not contain the aliphatic series radical of C1-C22 which do not contain a hydrogen atom, and a hydrogen atom. X3 shows the IVA group atom except carbon, VA group atom except nitrogen, or the VIA group atom except oxygen. n5 shows 0 or 1.

General formula (III)

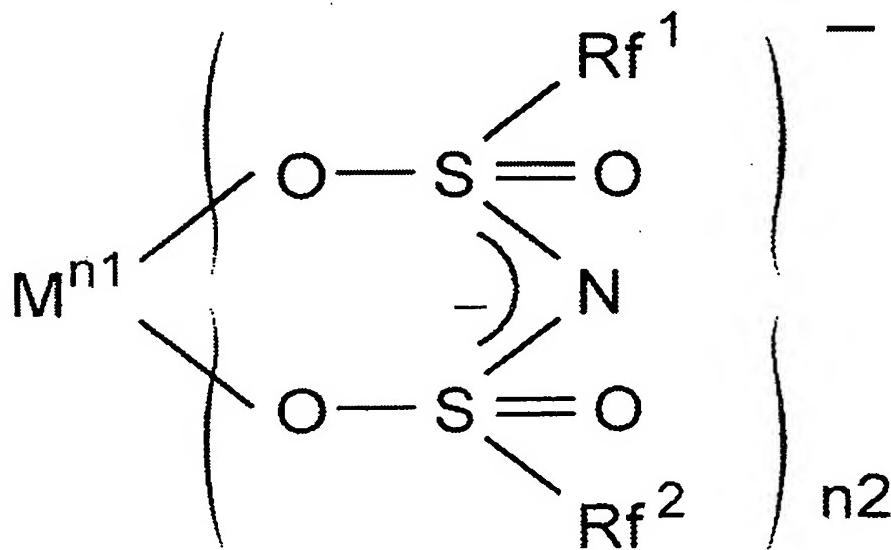
[Formula 10]



(In this formula, Rf¹, Rf², n₁, and n₂ are as aforementioned.)

General formula (IV)

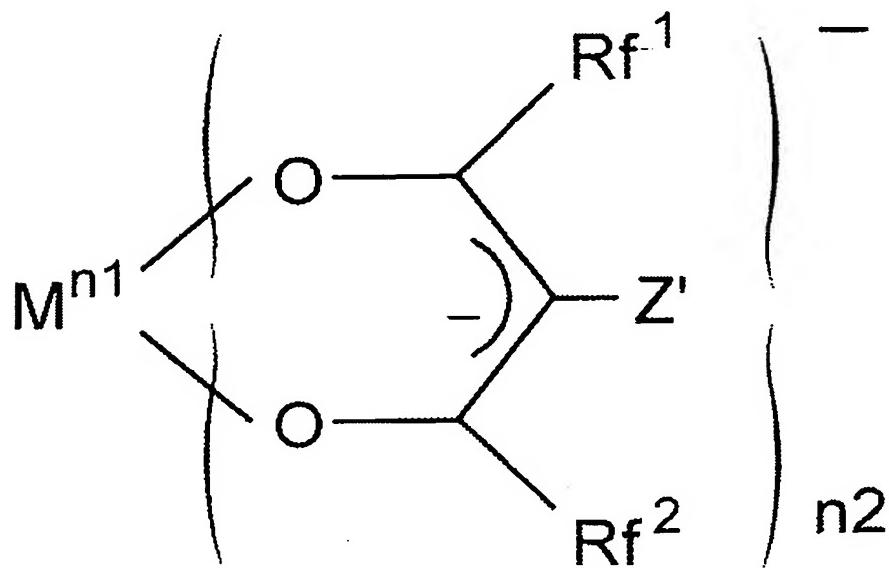
[Formula 11]



(In this formula, Rf¹, Rf², n₁, and n₂ are as aforementioned.)

General formula (V)

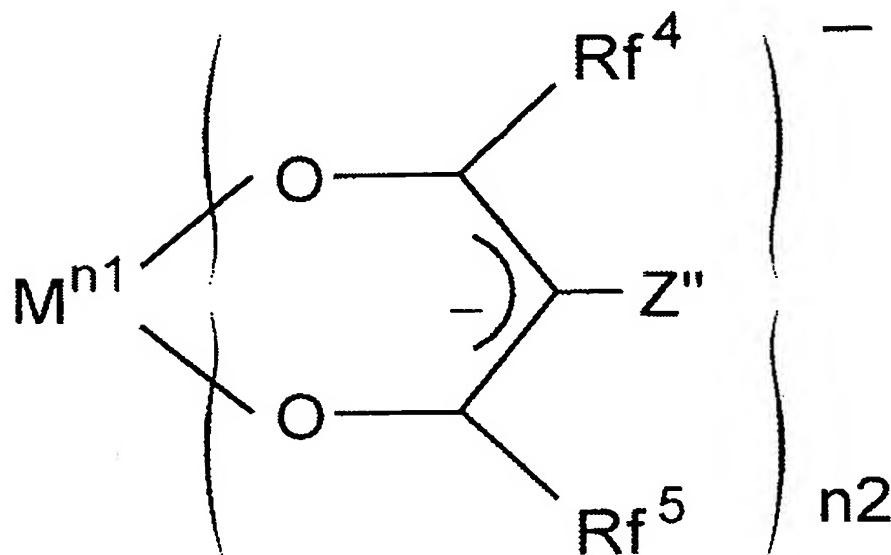
[Formula 12]



(In this formula, $Rf1$, $Rf2$, $n1$, $n2$, and Z' are as aforementioned.)

General formula (VI)

[Formula 13]

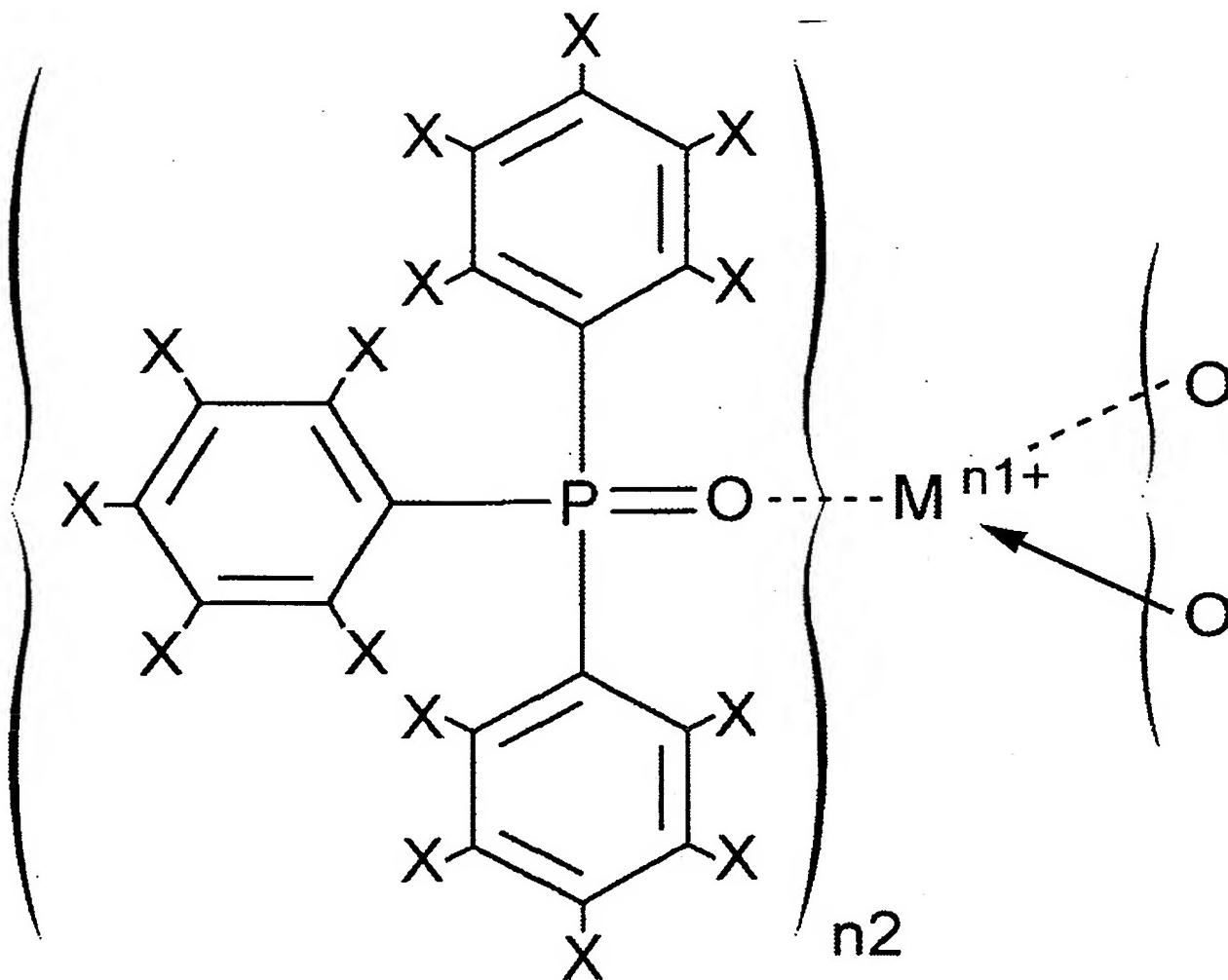


(In this formula, $n1$ and $n2$ are as aforementioned.) Z'' shows a hydrogen atom or Z' (Z' is the same as the above).

$Rf4$ and $Rf5$ show the same or the heterocycle radical which does not contain the different aromatic series radical or different hydrogen atom which does not contain the aliphatic series radical of C1-C22 which do not contain a hydrogen atom, and a hydrogen atom.

General formula (VII)

[Formula 14]



(In this formula, n_1 shows 2 or 3.) n_2 shows 1 or 2. n_3 shows 1, 2, 3, or 4. X shows the same or a different hydrogen atom, a heavy hydrogen atom, a halogen atom, the radical of C1-C20, a hydroxyl group, a nitro group, the amino group, a sulfonyl group, a cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulfhydryl group. Y shows the same or a different radical of C1-C20, a hydroxyl group, a nitro group, the amino group, a sulfonyl group, a cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulfhydryl group. Z shows a hydrogen atom or a heavy hydrogen atom.

[Procedure amendment 5]

[Document to be Amended] Description

[Item(s) to be Amended] 0022

[Method of Amendment] Modification

[The content of amendment]

[0022]

In addition, in these rare earth complexes, Rf1 and Rf2 are good in respect of compatibility with plastics and the polymer whose thing to C1 or about two C is the below-mentioned transparency fixed support, and they generate a polymer with stable CF₃ or CF₂CF₃ especially also in it.

[Translation done.]